

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Organosilicon Compounds and processes for their production

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We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of Roscoe Adams Pike), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

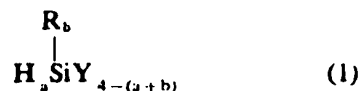
This invention relates to a process for producing organosilicon compounds. More particularly, this invention relates to a process for producing gamma-chloroisobutylhalosilanes. This invention further provides processes for producing silicon compounds containing a silicon bonded gamma-aminoisobutyl group by reacting ammonia, a primary or a secondary organic amine and a silicon compound containing a silicon bonded gamma-chloroisobutyl group.

The present invention provides a process for producing high yields of gamma-chloroisobutylhalosilanes. The present invention is based on the discovery that good yields of gamma-chloroisobutylhalosilanes are produced by the platinum-catalyzed reaction of methylal chloride and hydrogenchlorosilanes only when the reaction is conducted under conditions such that local overheating or hot spots in the reaction zone caused by the heat of reaction are avoided. This discovery is unexpected since, when allyl chloride and hydrogenhalosilanes are reacted in the presence of an elemental platinum catalyst under conditions such that local overheating in the reaction zone is avoided, good yields of gamma-chloropropylhalosilanes are not produced.

This invention provides a process for producing gamma-chloroisobutylhalosilanes which involves reacting methylal chloride

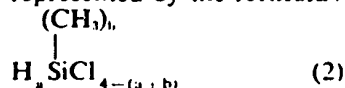
and a hydrogenhalosilane in the presence of a platinum catalyst, at a temperature from 45 15°C. to 190°C. and under conditions such that local overheating in the reaction zone is avoided.

The starting hydrogenhalosilanes employed in the invention are represented by the formula:



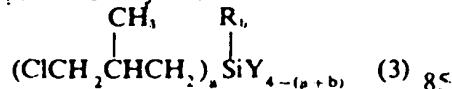
wherein R is a monovalent hydrocarbon group free from aliphatic unsaturation such as an alkyl group (for example, a methyl, ethyl, propyl or butyl group), an aryl group (for example, a phenyl group) or an aralkyl group (for example, a benzyl or a beta-phenylethyl group); a has a value of 1 or 2, b has a value from 0 to 2, (a + b) has a value from 1 to 3 and Y is a halogen atom, preferably a chlorine atom. The monovalent hydrocarbon groups represented by R preferably contain from 1 to 18 carbon atoms. In formula (1), R can represent the same or different groups.

A preferred class of starting hydrogenhalosilanes are those represented by the formula:



wherein a, b and (a + b) have the meanings defined for formula (1). Illustrative of the silanes represented by formula (2) are trichlorosilane, methyldichlorosilane and dimethylchlorosilane.

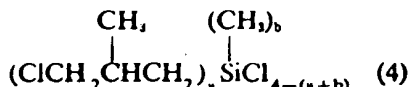
The gamma-chloroisobutylhalosilanes produced according to the process of this invention are represented by the formula:



wherein R, a, b, (a + b) and Y have the

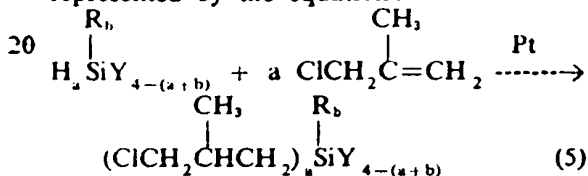
meanings defined for formula (1).

The starting silanes represented by formula (2) are converted by the process of this invention to silanes represented by the formula:



wherein a, b and (a + b) have the meanings defined for formula (1). Illustrative of the silanes represented by formula (4) are gamma-chloroisobutyltrichlorosilane, gamma-chloroisobutyl(methyl)dichlorosilane and gamma-chloroisobutyldimethylchlorosilane.

Methyl chloride and the starting hydrogenhalosilanes employed in this invention react via an addition reaction that can be represented by the equation:



wherein R, Y, a, b and (a + b) have the above-defined meanings.

Since the reaction represented by equation (5) is exothermic, local overheating or hot spots tend to occur in the reaction zone. Such local overheating produces undesirable side reactions that result in a significant decrease in the yield of the desired gamma-chloroisobutylhalosilanes. According to this invention local overheating is minimized and, consequently, unexpectedly high yields of the desired silanes are realized. Various means can be employed to avoid local overheating in the reaction zone, e.g. cooling coils can be provided in the reaction vessel or preferably, the reaction can be conducted within an inert liquid organic compound solvent in which methallyl chloride, the starting silane and the desired gamma-chloroisobutylhalosilane are mutually soluble or both such means can be employed.

Suitable solvents within which the reaction represented by equation (5) can be conducted include hydrocarbons such as benzene, toluene, cyclohexane and heptane and ethers such as isopropyl ether, diphenyl ether and dimethyl "Cellosolve" (Registered Trade Mark) (i.e. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$). The preferred solvents are chlorine-substituted olefins such as tetrachloroethylene and trichloroethylene. Gamma-chloroisobutylhalosilanes are soluble in these solvents and can be separated from them at the end of the reaction by any suitable means e.g. by fractional distillation. The amount of these solvents employed can vary from 0.1 up to 20 parts by weight, or preferably from 0.5 up to 10 parts by weight of the solvent per part by weight of the starting silane and methallyl chloride. Other amounts of the solvent can

be used since no particular amount is narrowly critical but best results are obtained by adhering to the indicated ranges. By way of illustration, low yields of gamma-chloropropyltrichlorosilane are produced by reacting trichlorosilane and allyl chloride whether or not such a solvent is employed.

The methallyl chloride and the starting silane can be heated to initiate the reaction represented by equation (5). Thereafter the heat of reaction or external heating can be used to promote the reaction. However, according to this invention the reaction represented by equation (5) is conducted at temperatures from 15°C. to temperatures as high as 190°C. with precautions taken to avoid local overheating in the reaction zone. Other temperatures are undesirable since the reaction rate is excessively slow at temperatures below 15°C. and since at temperatures about 190°C. undesirable side reactions occur to an extent that significantly decreases the yield of the desired silane. The pressure employed in the reaction represented by equation (5) may be subatmospheric, atmospheric or superatmospheric. Because of the volatility of some of the starting silanes, subatmospheric pressures are usually not desirable and superatmospheric pressures are preferred.

Stoichiometric amounts of the reaction are preferred in the reaction represented by equation (5). An excess of either reaction can be used but results in no particular gain. Incremental addition of one of the reactants to a reaction vessel containing the total amount of the other reactant to be used aids in preventing local overheating.

An elemental platinum catalyst is used in the reaction represented by formula (5). The platinum catalysts can be supported on such materials as charcoal, asbestos or silica gel. The preferred catalyst is platinum supported on the gamma allotrope of alumina. The amount of platinum used is not narrowly critical and can vary from 0.001 part to 5.0 parts by weight of platinum per 100 parts by weight of the starting methallyl chloride and the starting silane. The preferred amount of the catalyst depends on the type of catalyst used. When the catalyst is platinum supported on the gamma allotrope of alumina, the preferred amount of catalyst is 2 parts by weight of the mixture of platinum and alumina per 100 parts by weight of the starting silane and methallyl chloride, the mixture containing 2 parts by weight of platinum per 100 parts by weight of the alumina.

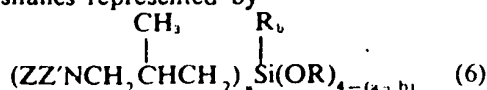
Polymerization inhibitors, such as 2,6-di-tert-butyl 4-methyl phenol, can be added to the reaction mixtures used in producing gamma-chloroisobutylhalosilanes in order to minimize vinyl-type polymerization side reactions that may occur. However, such side

reactions do not occur to any significant extent even when no polymerization inhibitor is present in the reaction mixture.

The gamma-chloroisobutylhalosilanes produced according to the process of this invention can be converted to various useful materials, that is, they can be converted to siloxanes containing gamma-chloroisobutyl-siloxy groups, to gamma-aminoisobutyl-
10 hydrocarbonoxysilanes and to siloxanes containing gamma - aminoisobutylsiloxy groups. Linear siloxanes containing gamma-chloroisobutylsiloxy groups are useful as lubricants. Resinous siloxanes containing
15 gamma-chloroisobutylsiloxy groups can be employed in molding and laminating compositions to produce molded products and laminates. Gamma-aminoisobutylhydrocar-
20 bonoxysilanes and siloxanes containing gamma-aminoisobutylsiloxy groups can be employed as corrosion inhibitors for metals such as iron that are in contact with aqueous
liquids, as chelating agents for copper and iron ions and in forming protective coatings
25 for metals such as iron.

Gamma-chloroisobutylhalosilanes are converted to siloxanes containing gamma-chloroisobutylsiloxy groups by hydrolysis and con-
30 densation procedures. The hydrolysis and condensation of these silanes can be conducted by forming a mixture of the silane and an organic solvent such as one of the above-described liquid organic compounds
used in producing gamma-chloroisobutyl-
35 halosilanes and slowly adding water to this mixture while agitating the mixture. The temperature is maintained at from 0°C. to 40°C. during the addition of the water. subatmospheric pressures are useful to aid
40 in the evolution of the hydrogen halide gas formed in the hydrolysis reaction. After the water has been added and the hydrolysis reaction has gone to completion, the mixture can be heated to from 40°C. to 150°C. to
45 complete the condensation reaction. Hydrocarbylhalosilanes (for example, dimethyldichlorosilane) can be cohydrolyzed and cocondensed with gamma-chloroisobutyl-
50 halosilanes as described above to produce siloxanes containing both gamma-chloroisobutylsiloxy groups and hydrocarbylsiloxy groups (for example, dimethylsiloxy groups).

Gamma-chloroisobutylhalosilanes are converted to gamma-aminoisobutylhydrocarbon-
55 oxysilanes represented by

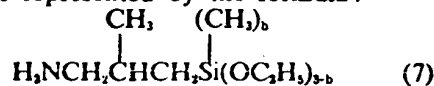


wherein R is a monovalent hydrocarbon
60 group free from aliphatic unsaturation, a has a value of 1 or 2, b has a value from 0 to 2 and (a+b) has a value from 1 to 3, Z is a hydrogen atom or a monovalent hydrocarbon group, Z' is a hydrogen atom
65 or a monovalent hydrocarbon group or when

a is 1 is a $\begin{array}{c} \text{CH}_3 \quad \text{R}_b \\ | \quad | \\ -\text{CH}_2\text{CHCH}_2\text{Si(OR)}_{3-b} \end{array}$ group.

Illustrative of the monovalent hydrocarbon groups represented by Z, Z' and R in formula
70 (6) are the alkyl groups (for example, methyl, ethyl, propyl and butyl groups), the aryl groups (for example, the phenyl group) and the aralkyl groups (for example the benzyl
75 and beta-phenylethyl groups). These monovalent hydrocarbon groups preferably contain from 1 to 18 carbon atoms. Illustrative of the isobutylsilane grouping of Z' are
80 $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$. In formula (6), Z and Z' can represent the same or different groups and R can represent the same or different groups.

A preferred class of gamma-aminoisobutylhydrocarbonoxysilanes of this invention
85 are those represented by the formula:



wherein b has a value from 0 to 2.
90

Illustrative of the gamma-aminoisobutylhydrocarbonoxysilanes of this invention are gamma-aminoisobutyltriethoxysilane, gamma-aminoisobutyl(methyl)diethoxysilane, gamma-aminoisobutyl (phenyl) dimethoxysilane,
95 gamma - aminoisobutyl(beta - phenylethyl) - dipropoxysilane, gamma - aminoisobutyl dimethylethoxysilane, gamma - aminoisobutyl-diphenyl(phenoxy)silane, di(gamma-aminoisobutyl)diethoxysilane, N-methyl-gamma-aminoisobutyltriethoxysilane, N,N-dimethyl-
100 gamma-aminoisobutyl(methyl)diethoxysilane, N-methyl - N - phenyl-gamma-aminoisobutyl(methyl)diethoxysilane or N,N-diphenyl-gamma-aminoisobutyltriethoxysilane.
105

The gamma-aminoisobutylhydrocarbonoxysilanes are produced by a procedure that involves an esterification reaction that includes reacting gamma-chloroisobutylhalosilane and an alcohol (for example, ethanol)
110 or phenol to produce a gamma-chloroisobutylhydrocarbonoxysilane and an amination reaction that includes reacting the gamma-chloroisobutylhydrocarbonoxysilane and ammonia, a primary amine or a secondary
115 amine to produce a gamma-aminoisobutylhydrocarbonoxysilane. The esterification reaction can be conducted by maintaining stoichiometric amounts of the starting materials at 0°C. to 50°C. to produce the
120 desired silane. The amination reaction can be conducted by reacting the gamma-chloroisobutylhydrocarbonoxysilane and a compound represented by the formula:



wherein Z has the meaning defined for formula (6) at a temperature of from 100°C. to 200°C.

The starting compounds represented by formula (8) used in producing the gamma-
130

aminoisobutylhydrocarbonoxysilane of this invention include ammonia and primary and secondary organic amines such as aryl amines (for example, aniline and diphenylamine), alkyl amines (for example, methyl amine, dimethyl amine, ethyl amine, diethyl amine and methyl ethyl amine) and alkyl aryl amines (for example, methyl phenyl amine). The preferred starting compound 10 represented by formula (8) is ammonia.

The relative amount of the reactants used in producing the silanes of this invention are not narrowly critical. In general, it is desirable to employ an excess of the compound represented by formula (8) in the reaction mixture in order to insure that the gamma-chloroisobutylhydrocarbonoxysilane is completely converted to the desired product. Thus, in the case of ammonia, from 15 5 to 60 moles in excess of the amount stoichiometrically required to convert the starting silane to the desired product is useful but a 10 to 30 mole excess is preferred. No commensurate advantage is gained by 25 employing other amounts of reactants. The above-indicated relative amounts of the reactants refers to the total amounts of the reactants used in the reaction. During the course of the reaction the ammonia or the 30 amine is preferably added by periodically adding small increments of the starting silane to a vessel containing total amount of the ammonia or organic amine to be used.

The amination reaction is preferably conducted within a liquid organic compound solvent in which the starting compounds are mutually soluble. Suitable solvents include polar liquids such as alcohols and non-polar liquids such as ethers, halohydrocarbons and 40 hydrocarbons. Polar solvents, especially ethanol, are often preferred since the rate of the reaction is faster in such solvents than in non-polar solvents. However, mixtures of polar and non-polar solvents are useful (for 45 example, a mixture of ethanol and isopropyl ether) since the hydrochloride salts formed as by products ($-\text{NH}\cdot\text{HCl}$) in the reaction

precipitate from such mixtures in a coarse, 50 crystalline form that facilitates separating these salts from the product-solvent solution, e.g. by filtration. The amines formed are usually soluble in the solvents employed. The solvents are readily separated from the 55 amines by distillation. From 10 parts to 150 parts by weight of the solvent per 100 parts by weight of the reactants are useful but from 25 to 125 parts of solvent per 100 parts by weight of the reactants are preferred. 60 Although other amounts of solvent can be used, no commensurate advantage is usually gained thereby.

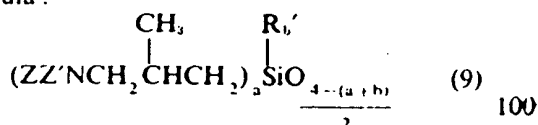
It is highly desirable to maintain anhydrous conditions during the production of the 65 silanes of this invention. Even traces of water

promote undesirable side reactions that decrease the yield of the desired products.

Temperatures from 100°C. to 200°C. and times from 5 hours to 36 hours are advantageously used in producing the silanes of 70 this invention represented by formula (6). However, temperatures from 150°C. to 175°C. and times from 7 hours to 20 hours are preferred. Generally, the time required 75 for the reaction decreases as the temperature employed is increased. When ammonia or volatile organic amines are used as reactants, it is desirable to conduct the reaction represented by equation (5) at super-atmospheric 80 pressure, especially when elevated temperatures are used. However, the particular temperature, time or pressure employed can be varied outside of those indicated but no commensurate advantage is gained thereby.

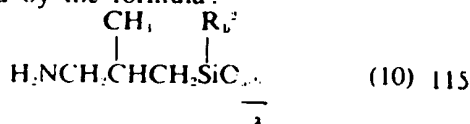
A hydrochloride of the starting compound 85 represented by formula (8) can be added to the reaction mixture used in producing the silanes of this invention in order to reduce somewhat the amount of by products formed in the reaction. By way of illustration, when 90 ammonia is employed as a reactant, ammonium chloride can be added to the initial reaction mixture.

The siloxanes of this invention contain at least one group that is represented by the 95 formula:



wherein R' is free from aliphatic unsaturation and is a monovalent hydrocarbon group (i.e. the above-defined R group) or a hydrocarbonoxy group (i.e. an $-\text{OR}$ group where R has the above-defined meaning) and Z, 105 Z', a, b and (a + b) have the meanings defined for formula (6). These siloxanes can have linear, cyclic or branched structures.

A preferred class of siloxanes of this invention 110 are those that contain at least one group represented by the formula:

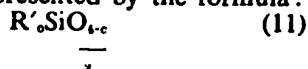


wherein R² is a methyl or an ethoxy group and b has a value from 0 to 2.

Illustrative of the siloxane groups represented by formula (9) are the gamma-aminoisobutylsiloxo, gamma-aminoisobutyl- 120 (methyl)siloxo, gamma-aminoisobutyl-(methyl)ethoxysiloxo, gamma-aminoisobutyl-diphenylsiloxo, gamma-aminoisobutyl- 125 (ethoxy)siloxo, gamma-aminoisobutyl-diethoxysiloxo, gamma-aminoisobutyl(beta-phenylethyl)siloxo, gamma-aminoisobutyl-dimethylsiloxo, di(gamma-aminoisobutyl)siloxo, N-methyl-gamma-aminoisobutylsiloxo, N,N- 130

dimethyl - gamma - aminoisobutyl(methyl) - siloxy, N-phenyl-gamma-aminoisobutyl-(phenyl)siloxy and N-phenyl-gamma-aminoisobutyl(methyl)siloxy groups.

- 5 The siloxanes of this invention include those which contain, in addition to at least one group represented by formula (9), at least one group represented by the formula:

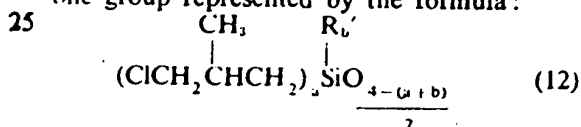


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wherein R' has the meaning defined for formula (9) and c has a value from 1 to 3. Illustrative of the siloxane groups represented by formula (11) are the methylsiloxy,

- 15 dimethylsiloxy, trimethylsiloxy, phenyl(methyl)siloxy, beta - phenylethylsiloxy, diethylsiloxy, methyl(ethyl)siloxy, diphenylsiloxy and triphenylsiloxy groups. These siloxanes can also contain SiO₂ groups.

- 20 The siloxanes of this invention are produced by reacting ammonia or a primary or secondary organic amine represented by formula (8) and a siloxane containing at least one group represented by the formula:



- 30 wherein R', a, b and (a + b) have the meanings defined for formula (9).

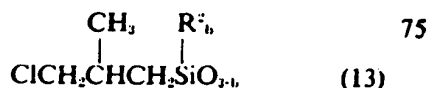
The siloxanes of this invention may also be produced by hydrolysis of a gamma-aminoisobutylhydrocarbonoxysilane represented by formula (6).

- 35 The starting siloxanes used in producing the siloxanes of this invention can contain, in addition to at least one group represented by formula (12), groups represented by formula (11). These starting siloxanes can be produced by reacting a gamma-chloroisobutylhalosilane (along with, if desired, hydrocarbon halosilanes) with water to effect the hydrolysis and condensation of the silane to produce a siloxane containing group represented by formula (12). Alternatively, these starting siloxanes can be produced by hydrolyzing and condensing the gamma-chloroisobutylhydrocarbonoxysilanes along with, if desired, silanes that have the formula R'Si(OR)_c, where R has the meaning defined for formula (6) and R' and c have the meanings defined for formula (11).

- 40 Illustrative of the starting siloxanes used in producing the siloxanes of this invention are cyclic siloxanes composed of gamma-chloroisobutyl(methyl)siloxy groups (such as gamma-chloroisobutyl(methyl)siloxane cyclic trimer and tetramer), end-blocked linear siloxanes such as a siloxane composed of gamma-chloroisobutyl(phenyl)siloxy groups end-blocked by gamma-chloroisobutyl dimethylsiloxy groups, disiloxanes such as bis-(gamma - chloroisobutyl)tetramethyldisiloxane, resinous siloxanes composed of

gamma-chloroisobutylsiloxy groups (i.e. CH₃

CICH₂CHCH₂SiO_{1.5}), and siloxanes composed of gamma-chloroisobutyl(ethoxy)siloxy 70 and phenyl(ethoxy)siloxy groups. The preferred starting siloxanes are those containing at least one group represented by the formula:



75

wherein R² and b have the meanings defined for formula (10).

The conditions used in producing the gamma - aminoisobutylhydrocarbonoxysiloxanes of this invention, by reacting a gamma-chloroisobutylhydrocarbonoxysiloxane and 85 ammonia, a primary or a secondary organic amine, (e.g. the ratio of reactants, solvents, temperature, pressure and time) are the same as the conditions outlined above for the production of the gamma-aminoisobutylhydrocarbonoxysilanes of this invention.

The resulting silanes and siloxanes of this invention were found to be far superior to known aminoalkyl silicon compounds in various applications. By way of illustration, 95 the gamma-aminoisobutyltriethoxysilanes of this invention were found to be remarkably superior to known delta-amino-n-butyltriethoxysilanes in sequestering iron and copper ions. As a further illustration, coatings on 100 iron surfaces composed of copolymers of this invention containing both gamma-aminoisobutylsiloxy and phenylsiloxy groups were found to be outstandingly superior to coatings composed of copolymers containing 105 delta-amino-n-butylsiloxy and phenylsiloxy groups in protecting iron from corrosion in aerated sodium salt solutions.

Those compounds of this invention that contain nitrogen-bonded hydrogen atoms (i.e. primary and secondary amines) can be reacted via these hydrogen atoms with organic compounds containing, for example, carboxy and acid halide groups to form useful derivatives. The primary amines of this invention, owing to the presence of two such hydrogen atoms on each nitrogen, are particularly suited for such reactions and so are particularly useful materials. The secondary amines of this invention are useful to a 120 lesser extent in forming derivatives by such reactions.

The compounds of this invention are useful per se as lubricating oils. These compounds can also be used as sizes and finishes 125 for fibrous materials, such as glass fibers, that are used along with organic resins in producing laminates. The compounds of this invention can further be blended with or reacted with (e.g. as by equilibration) other 130

organosilicon compounds to incorporate amino functional groups therein.

As used herein, the term "hydrocarbyl" denotes a monovalent group composed only of carbon and hydrogen (e.g. the ethyl and phenyl groups) and the term "hydrocarbon-oxy" denotes a monovalent group composed of a hydrocarbyl group linked to an oxygen atom (e.g. the ethoxy and phenoxy groups). The following examples illustrate the present invention:

Example I

Into a 1-liter, 3-necked flask equipped with reflux condenser, mechanical stirrer, and dropping funnel were charged 115 g (1 mole) of $\text{CH}_3\text{SiHCl}_2$, 200 cc. of trichloroethylene and 4.1 g platinum-on-gamma-alumina catalyst (2 parts by weight platinum per 100 parts by weight of gamma-alumina). The mixture was heated with stirring until the $\text{CH}_3\text{SiHCl}_2$ started to reflux (40-45°C.) and 90.5 (1 mole) of methallyl chloride was then added by means of the dropping funnel in small increments over a 2.5 hr period. The reaction was very exothermic. After the addition was complete the mixture was heated at 80°C. for an additional hour. The mixture was then cooled, filtered to remove the catalyst, and the solvent was evaporated from the filtrate under reduced pressure. The residue was fractionated through a glass-helix packed column under reduced pressure to give 163 g. (80 mole-% yield) of $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$, b.p. 59°C. (at 5.0 mm.), n_D^{25} 1.4617. The compound was identified by infra-red spectrum and elemental analysis:

Calculated for $\text{C}_4\text{H}_{11}\text{SiCl}_3$: Si, 13.65 wt-%; Cl, 51.9 wt-%

Found: Si, 12.4 wt-%; Cl, 52.1 wt-%

Example II

Methallyl chloride (1 mole) and $\text{CH}_3\text{SiHCl}_2$ (1.5 moles) were reacted under the conditions used in Example I employing trichloroethylene as a solvent and platinum-on-gamma-alumina as a catalyst. A 98 mole-% yield of $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ was obtained.

Example III

Into a 3-liter steel pressure vessel was charged 447 g. (3.3 mole) of HSiCl_3 , 241.5 g. (2.66 mole) of methallyl chloride, 14.0 g. of platinum-on-gamma-alumina (2 parts by weight of platinum per 100 parts by weight of gamma-alumina), 7.0 g. of 2,6-di-tert-butyl 4-methyl phenol (1 wt-percent) and 330 cc. of trichloroethylene. The vessel was sealed and heated, with rocking, at 175°C. for 4 hrs. The vessel was then cooled and the products were discharged and filtered. The crude product concentrated under reduced pressure. The residue was distilled through a glass-helix packed column to give 450 g. (76 mole-% yield) of $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$, b.p. 43-44°C. (1.2 mm.), n_D^{25} 1.4660.

The compound was identified by infra-red analysis and hydrolyzable chlorine. [Theory: wt-% Cl = 47.0; Found: wt-% Cl = 46.8].

Examples I to III illustrate that high yields of the desired silanes (76%-98%) are produced when methallyl chloride and hydrogenhalosilanes are reacted within a suitable solvent employing a platinum catalyst according to the practice of this invention.

Example IV

Into a 300-cc. steel pressure vessel were charged 135.5 g. HSiCl_3 , 90.5 g. methallyl chloride, and 1 g. of platinum-on-charcoal (one part by weight of platinum per 100 parts by weight of charcoal). No solvent was employed. The vessel was sealed and heated with rocking to 175°C. At this point an exothermic reaction occurred and the temperature momentarily rose to 205°C. The temperature was maintained at 175°C. for 4.5 hrs. The 212 g. of product so obtained was filtered and distilled to give 120 g. (53 mole-% yield) of $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SiCl}_3$, b. p. 190-193°C.

Chemical Analysis:

Calculated for $\text{C}_4\text{H}_9\text{SiCl}_3$: C, 21.2 wt-%; H, 3.5 wt-%; 12.4 wt-%

Found: C, 21.9 wt-%; H, 3.8 wt-% Si, 12.1 wt-%

A comparison of the yield of the desired silane obtained in this Example with the yields obtained in Examples I, II and III illustrates the improvement consequent upon the avoidance of local over heating in the reaction vessel by the use of a solvent.

Example V

Into a one liter, 3-necked flask that was equipped with a stirrer, a reflux condenser and a dropping funnel were charged 57.5 g. (0.5 mole) of $\text{CH}_3\text{SiHCl}_2$, 2.16 (2 wt-%) of platinum-on-gamma-alumina (containing 2 parts by weight of platinum per 100 parts by weight of the platinum and alumina) and 76 g. of n-heptane. The mixture was heated to reflux (45-50°C.) with stirring and 38 g. (0.5 mole) of allyl chloride was added in small increments over a period of about one hour. The mixture was then refluxed for another hour. The mixture was cooled and filtered and most of the solvent was distilled. The residue was fractionally distilled and 33.5 g. (35 mole-% yield) of $\text{Cl}(\text{CH}_2)_3\text{SiCH}_3$, Cl, (b.p. 37°C. at 0.2 mm) was obtained.

Example VI

When allyl chloride and $\text{CH}_3\text{SiHCl}_2$ were reacted according to the procedure used in Example V employing no solvent and platinum-on-gamma-alumina as a catalyst, a 30 mole-% yield of $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)\text{Cl}_2$ was obtained.

Example VII

Following the procedure used in Example V, allyl chloride and $(\text{CH}_3)_2\text{SiHCl}$ were reacted employing tetrachloroethylene as a solvent and platinum-on-gamma-alumina as

a catalyst. A 32 mole-% yield of $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{Cl}_2$ was obtained.

The results obtained in Example VI illustrate the low yields obtained in the production of chloroalkylhalosilanes by known processes. The results obtained in Example V and VII show that the low yields obtained when using allyl chloride are not significantly improved by conducting the reaction in a solvent.

Example VIII

A mixture was formed in a fifteen gallon nickel-lined autoclave that was equipped with internal cooling coils. The mixture contained methyldichlorosilane (32 pounds, 96.7% purity), methallyl chloride (17 pounds) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (2.84 grams) dissolved in ethanol (25 cc.). The reaction began at about 20°C. The temperature in the autoclave rose to 168°C. and the pressure rose to 225 psig. The reactants were cooled to 70°C. by passing a coolant through the cooling coils. The reactants were heated to 150°C. and maintained at 150°C. for 15 minutes. The pressure did not exceed 100 psig. The contents of the autoclave were cooled to 25°C. and a sample vacuum distilled to isolate gamma-chloroisobutyl(methyl)dichlorosilane (boiling point 52-55°C. at 4 mm of Hg). A 96.7% yield of the latter silane was obtained.

Example IX

A mixture was formed in a fifteen gallon nickel-lined autoclave that was equipped with internal cooling coils. The mixture contained methyldichlorosilane (24.75 pounds, 96.7% purity), methallyl chloride (17.0 pounds) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.42 g) dissolved in ethanol (25 cc). The reaction began at 20°C. and the temperature rose to 182°C. and the pressure rose to 225 psig. A coolant was continuously passed through the cooling coils and the temperature was lowered to 77°C. The reactants were heated to 150°C. and maintained at 150°C. for 10 minutes. The pressure did not exceed 100 psig (lbs per sq. in.). The contents of the autoclave were cooled to room temperature and a sample was vacuum distilled to isolate gamma-chloroisobutyl(methyl)dichlorosilane (88.7% yield).

Examples VIII and IX illustrate that high yields of gamma-chloroisobutylhalosilanes are produced in accordance with the practice of this invention when cooling coils are used to prevent local overheating in the reaction zone.

Example X

Gamma-chloroisobutyltriethoxysilane (1.0 mole, 254.5 g.), isopropyl ether (120 ml.), ethyl alcohol (360 ml.), and NH_4Cl (10 wt.-%, 25.5 g.) were charged to a nitrogen sparged 3-liter stainless steel pressure vessel which was then chilled in a Dry Ice-acetone mixture. Anhydrous ammonia (25.0 moles,

520 ml.) was liquefied and added to the vessel which was sealed and heated at 145°-155°C. for 16 hr. in a rocking electric furnace. The maximum pressure reached in the vessel was 1500 psi. After cooling to room temperature the NH_3 pressure was slowly released, by slowly opening a relief valve in the vessel, and the vessel opened. A mixture of water-white solution and white fluffy NH_4Cl was obtained. After filtration to remove the NH_4Cl the solvent was evaporated under reduced pressure and the residue so obtained was fractionated through a 30 cm. Vigreux column. The fraction boiling from 67°C. at 1.1 mm to 68°C. at 1.0 mm was identified as a primary amine having the formula: $\text{H}_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$, $[\text{n}_D^{25}, 1.4220]$. The fraction boiling from 100-136°C. at 1.0 mm was a secondary amine having the formula: $\text{HN}[\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3]$. The residue consisted of siloxanes containing primary and secondary aminoisobutyl groups formed by the hydrolysis and condensation of the primary and secondary aminoisobutylsilanes due to the presence of water in the system. The yield of the primary aminoisobutylsilane was 52.6% and the yield of the secondary aminoisobutylsilane was 18.6%.

Example XI

Gamma-chloroisobutyl(methyl)diethoxysilane (0.2 moles, 45.0 g), isopropyl ether (15 ml.) and ethyl alcohol (45 ml.) were charged to a 300 cc stainless steel pressure vessel which was chilled in a Dry Ice and acetone mixture. Anhydrous ammonia (5.0 moles, 104 ml.) was liquefied and added to the vessel which was sealed and heated at 160°C. for 10 hr. in a rocking, electric furnace. After cooling the pressure was vented and a clear light yellow solution was filtered from the solid NH_4Cl which had formed. The NH_4Cl was washed with 20 ml. of ethanol which was added to the filtrate. The NH_4Cl was washed out with water. The solvent was stripped under reduced pressure and the residue so obtained was fractionally distilled through a 30 cm Vigreux column. The fraction boiling from 46°C. at 0.6 mm to 50°C. at 0.7 mm $[\text{n}_D^{25}, 1.4278]$ was identified as the primary

amine, $\text{H}_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_2$, and the fraction boiling from 112°C. at 0.8 mm to 118°C. at 0.9 mm $[\text{n}_D^{25}, 1.4387]$ was identified as the secondary amine, $\text{HN}[\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_2]$. No residue remained after the fractional distillation, indicating that no tertiary amine had been formed.

Example XII

The procedure followed in Example XI was repeated and a 61.4% yield of the

primary aminoisobutylsilane and a 16.5% yield of the secondary aminoisobutylsilane were produced. Siloxanes containing primary and secondary aminoisobutyl groups were also formed by hydrolysis of these aminoisobutylsilanes due to the presence of water in the system.

Example XIII

Gamma-aminoisobutyltriethoxysilane (6.8 g.) was added to 100 ml. of water with rapid stirring. The solution was shaken for 1 hour at room temperature and then the water was stripped under reduced pressure leaving a white resinous solid as a residue. The residue was heated at 100°C. for 1 hour under reduced pressure. A white brittle solid (3.2 g.) that dissolved slowly in water was obtained. The solid was found to contain 0.4 wt-% ethoxy groups and was a siloxane polymer composed predominantly of groups having the formula: $H_2NCH_2CH(CH_3)CH_2SiO_{1.4}$ with some groups having the formula: $H_2NCH_2CH(CH_3)CH_2Si(OC_2H_5)_nO_{2.4}$ where d

has a value from 1 to 2.

Example XIV

In a 50 ml flask was charged 20 g. of $CH_3NH_2CH_2CH(CH_3)CH_2Si(OEt)_3$ and 18 cc of distilled water (10 mole excess). A short Vigreux column was attached to the flask and heat applied to drive off water and the ethanol formed. The flask was heated to 150°C. over a period of 1 hour. The mixture was then stripped under reduced pressure and the residue so produced was refluxed in toluene (75 ml.) for 5 hours, to remove any remaining water as an azeotrope. The toluene was evaporated under reduced pressure to give 11.2 g. of a colorless oil. Infra-red spectrum identified the oil as mainly the tetramer, $[NH_2CH_2CH(CH_3)CH_2Si(CH_3)_2O]_4$ with a trace of trimer present. The elemental analysis of the tetramer gave the following results:

Theory (wt-%): N, 10.7; Si, 21.4

Found (wt-%): N, 9.0; Si, 21.4

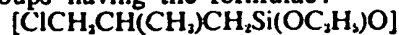
Example XV

Into a 300 cc. stainless steel pressure vessel cooled with Dry Ice were charged 37.6 g. (0.26 mole) of a siloxane composed of groups having the formula $[CICH_2CH(CH_3)CH_2Si(CH_3)_2O]$ and containing about 1.5 wt-% silicon bonded hydroxy groups, 15 ml. isopropyl ether, 45 ml. absolute ethanol, 5 g. of ammonium chloride and 100 ml. of liquid ammonia. The vessel was sealed and heated with rocking at 160°C. for 10 hr. After cooling, the excess ammonia was vented and the contents of the vessel filtered to give 15 g. of NH_4Cl . The filtrate was stripped of solvent to give 20 g. of an oil. The infra-red spectrum of the oil showed it to be a mixture of cyclic

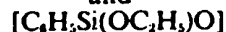
siloxanes having the formula $[NH_2CH_2CH(CH_3)CH_2Si(CH_3)_2O]_x$ where x has an average value of about 4.

Example XVI

A copolymer composed of equal numbers 70 of groups having the formulae:



and



(0.1 moles, 32.7 g.), isopropyl ether (15 ml.) 75 and ethyl alcohol (45 ml.) were charged to a 300 cc stainless steel pressure vessel which was chilled in a Dry Ice and acetone mixture. Anhydrous ammonia (100 ml.) was liquefied and added to the vessel which was sealed and heated at 170° C. for 12.5 hours in a rock- 80 ing electric furnace. After cooling the excess NH_3 was bled down and the vessel opened. A mixture of straw yellow solution and white fluffy NH_4Cl was obtained. After filtration 85 to remove the NH_4Cl , the solvent was evaporated on a rotary evaporator to 74 per cent solids. A small sample was stripped of solvent and the solid so obtained submitted for elemental analysis which gave the follow- 90 ing results:

Found: N = 4.4

Calc for the primary amine: N = 4.9

A sample of the solid was also submitted for infra-red survey. Strong absorption due 95 to NH_2 , $SiOEt$, $SiOSi$, SiC_6H_5 , CH_3 and CH_2 groups were found. The analysis indicated that the product was a copolymer composed of equal numbers of groups having the



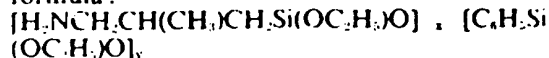
and



Example XVII

A copolymer with the average formula: 105 $[CICH_2CH(CH_3)CH_2Si(OC_2H_5)_2O]_x[C_6H_5Si(OC_2H_5)_2O]_y$

where $x = y$ (37.6 g.), isopropyl ether (15 ml.) and ethyl alcohol (45 ml.) were charged to a 300 cc stainless steel pressure vessel 110 which was chilled in a Dry Ice and acetone mixture. Anhydrous ammonia (100 ml.) was condensed and added to the vessel which was sealed and heated at 160°C. for 10 hr. After cooling the excess NH_3 was vented, the 115 vessel opened and NH_4Cl filtered from the solution. The solvent was stripped under reduced pressure to give a viscous solution (90 percent solids). A small quantity of the solution was stripped of solvent and the solid 120 residue was analyzed. The analysis showed that the solid was a copolymer of the formula:



The elemental analysis of the copolymer gave the following results:

Calc. (wt-%) N, 4.3; Si, 17.1

Found (wt-%) N, 4.3; Si 20.4

Example XVIII

Gamma-chloroisobutyltriethoxysilane (0.4 moles, 102.0 g.), ethyl alcohol (30 ml.) and isopropyl ether (10 ml.) were charged to a 300 cc. stainless steel pressure vessel. A mixture of monomethylamine and dimethylamine was added to the vessel which was chilled in a Dry Ice and acetone mixture. The vessel was sealed and heated in a rocking electric furnace at 150°C. for 13.5 hours during which time monomethylamine and dimethylamine hydrochlorides were formed and precipitated. The vessel was cooled and the amine hydrochlorides were removed from the solution by filtration. The solvent was stripped to give a large amount of gel-like material which was apparently the hydrochloride salts of the desired aminoalkylsilanes. The gel-like material was dissolved in benzene and triethylamine was added. Triethylamine hydrochloride precipitated and was removed by filtration. The solvent was stripped leaving an oil as a residue. The oil was fractionally distilled to separate the

secondary amine [i.e. $\text{CH}_3\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$; n_D^{25} , 1.4185; 33% yield] which distilled from 58°C. at 0.2 mm to 61°C. at 0.3 mm and the tertiary amine [i.e. $(\text{CH}_3)_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$; n_D^{25} , 1.4330; 30% yield] which distilled from 116°C. at 0.3 mm to 135°C. at 0.4 mm. The elemental analysis of these amines gave the following results:

	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OEt})_3 \end{array}$			
	N	Si	C	H
Calc. (wt-%)	5.6	11.25	53.0	9.65
Found (wt-%)	5.6	11.3	52.1	9.8
	$\begin{array}{c} \text{H} \\ \\ (\text{CH}_3)_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OEt})_3 \end{array}$			
	N	Si	C	H
Calc. (wt-%)	5.33	10.7	54.7	11.0
Found (wt-%)	5.4	13.2	53.4	10.1

Example XIX

The starting siloxanes used in producing the siloxanes of this invention can be produced by the following procedure. A gamma-chloroisobutylhalosilane that can be produced as described in Example X is dissolved in an organic solvent (e.g. trichloroethylene) and water is slowly added to the solution so formed. The mixture is agitated during the addition of the water and the temperature of the mixture is maintained at 0°C. to 40°C. Hydrogen chloride gas is formed and the maintenance of sub-atmospheric pressure aids in its removal. The mixture is then heated to 40°C. to 150°C. to produce a siloxane composed of groups represented by formula (9) which can be isolated by fractional distillation. Starting siloxanes containing both groups represented by formula (9) and groups represented by formula (8)

can be produced by employing both a silane (e.g. dimethyldichlorosilane or diphenyldichlorosilane) represented by the formula $\text{R}'_c\text{SiY}_{4-c}$, wherein R', Y and c have the above-defined meaning, and gamma-chloroisobutylhalosilanes in the above-described procedure.

Example XX

The following experiment was performed to compare the effectiveness of a compound of this invention [gamma-aminoisobutyltriethoxysilane, $\text{H}_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$] with a known aminoalkylsilane [delta-n-butyl-triethoxysilane, $\text{H}_2\text{N}(\text{CH}_2)_4\text{Si}(\text{OC}_2\text{H}_5)_3$] as sequestering agents for iron and copper ions.

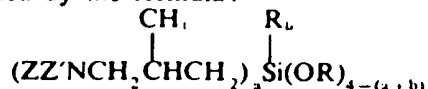
Aqueous solutions were formed containing the silane being tested (0.1 M), $\text{Fe}(\text{NO}_3)_3$ (0.1 M) or $\text{Cu}(\text{NO}_3)_2$ (0.1 M) and, when necessary to obtain a clear solution, nitric acid (0.1 M). The solutions were titrated with sodium hydroxide (0.1 M) until a precipitate formed. Since the tendency of such precipitates (i.e. hydroxide and/or complexes of Cu^{2+} or Fe^{3+}) increases with increasing pH, the pH at which these precipitates form in the presence of a sequestering agent is directly proportional to the effectiveness of the sequestering agent. Precipitates were obtained at the indicated pH with the silanes tested.

Silane Tested	Ion Sequestered	pH at which precipitation occurred
$\text{H}_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	Fe^{3+}	11.5
$\text{H}_2\text{N}(\text{CH}_2)_4\text{Si}(\text{OC}_2\text{H}_5)_3$	Fe^{3+}	10.0
$\text{H}_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	Cu^{2+}	10.0
$\text{H}_2\text{N}(\text{CH}_2)_4\text{Si}(\text{OC}_2\text{H}_5)_3$	Cu^{2+}	8.2

These results illustrate the superiority of the compounds of this invention as sequestering agents as compared to known aminoalkylsilicon compounds.

WHAT WE CLAIM IS:--

1. A gamma-aminoisobutylsilane represented by the formula:



wherein R is a monovalent hydrocarbon group free from aliphatic unsaturation, a is 1 or 2, b is 0, 1 or 2 and (a + b) is 1, 2 or 3, Z is a hydrogen atom or a monovalent hydrocarbon group and Z' is a hydrogen atom or a monovalent hydrocarbon group or when a is 1 is a $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{R})_3(\text{OR})_{3-b}$ group.

2. Gamma-aminoisobutyltriethoxysilane.

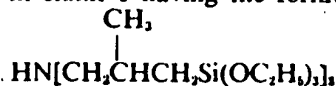
3. Gamma-aminoisobutyl (methyl) diethoxysilane.

4. Gamma-aminoisobutyldimethyl(ethoxy) silane.

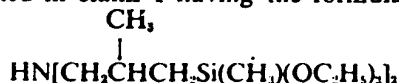
5. N-Methyl gamma-aminoisobutyltriethoxysilane.

6. N,N-Dimethyl gamma-aminoisobutyltriethoxysilane.

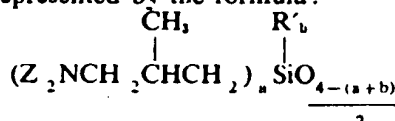
7. A gamma-aminoisobutylsilane as claimed in claim 1 having the formula:



8. A gamma-aminoisobutylsilane as claimed in claim 1 having the formula:

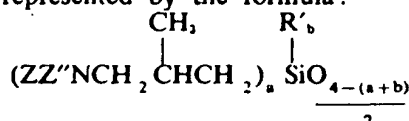


9. A siloxane containing at least one group represented by the formula:



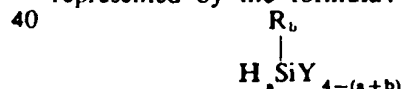
wherein Z is a monovalent hydrocarbon group or a hydrogen atom, R' is free from aliphatic unsaturation and is a monovalent hydrocarbon group or a hydrocarbonoxy group, a is 1 and b is 2.

10. A siloxane containing at least one group represented by the formula:

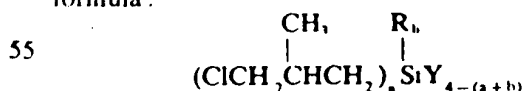


wherein Z is a monovalent hydrocarbon group or a hydrogen atom, Z' is an aryl group, R' is free from aliphatic unsaturation and is a monovalent hydrocarbon group or a hydrocarbonoxy group, a is 1 or 2, b is 0, 1 or 2, and (a+b) is 1, 2 or 3.

11. A process for producing organosilicon compounds, which comprises reacting methallyl chloride and a hydrogenhalosilane represented by the formula:



wherein R is a monovalent hydrocarbon group free from aliphatic unsaturation, Y is a halogen atom, a has a value from 1 to 2, b has a value from 0 to 2 and (a+b) has a value from 1 to 3, in the presence of an elemental platinum catalyst, at a temperature from 15°C. to 190°C. and under conditions such that local overheating in the reaction zone is avoided to produce a gamma-chloroisobutylhalosilane represented by the formula:



wherein R, Y, a, b and (a+b) have the above-defined meanings.

12. A process as claimed in claim 11, in which the reaction is carried out in an inert liquid organic compound, in which the methallyl chloride, the gamma-chloroisobutylchlorosilane and the hydrogenchlorosilane are mutually soluble.

13. A process as claimed in claim 12, in which the liquid organic compound is trichloroethylene.

14. A process as claimed in claim 11, 12 or 13, in which the platinum catalyst is elemental platinum supported on gamma-alumina.

15. A process as claimed in any of claims 11 to 14, in which the hydrogenhalosilane is methyldichlorosilane.

16. A process as claimed in any of claims 11 to 14, in which the hydrogenhalosilane is trichlorosilane.

17. A process as claimed in any one of claims 11 to 14, in which the hydrogenhalosilane is methyldichlorosilane.

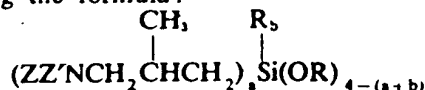
18. A process as claimed in any one of claims 11 to 17, in which the reaction is carried out in a reaction vessel containing cooling coils through which is passed a coolant to prevent local overheating in the reaction zone.

19. A process as claimed in claim 11 substantially as hereinbefore described in any one of Examples I to III, VIII or IX.

20. A process for producing organosilicon compounds, which comprises esterifying a gamma-chloroisobutylhalosilane produced by the process claimed in any of claims 11 to 16 and reacting the esterified product with a compound having the formula:



wherein Z is a hydrogen atom or a monovalent hydrocarbon group to produce a gamma-aminoisobutylhydrocarbonoxysilane having the formula:



wherein Z, Z', R, a and b have the meanings defined in claim 1.

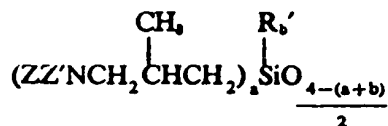
21. A process as claimed in claim 20, in which the intermediate gamma-chloroisobutylhydrocarbonoxysilane is reacted with ammonia dissolved in an anhydrous solution of an alcohol and an ether.

22. A process as claimed in claim 21, in which gamma-chloroisobutyltriethoxysilane is reacted with ammonia dissolved in an anhydrous solution of ethanol and isopropyl ether to produce gamma-aminoisobutyltriethoxysilane.

23. A process as claimed in claim 21, in which gamma-chloroisobutyl(methyl)diethoxysilane is reacted with ammonia in an anhydrous solution of ethanol and isopropyl ether.

24. A process as claimed in claim 20 substantially as hereinbefore described in any one of Examples X to XII and XVIII.

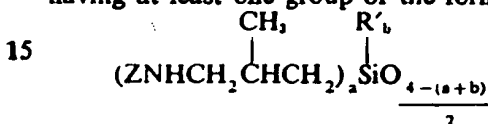
25. A process for producing a siloxane having at least one group of the formula:



wherein R' has the meaning defined in claim 5 9 and Z, Z', a and b have the meanings defined in claim 1 which comprises hydrolyzing a gamma-aminoisobutylhydrocarbonoxysilane claimed in claim 1.

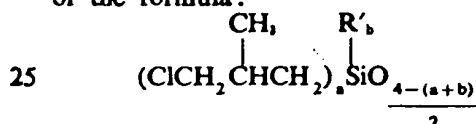
26. A process as claimed in claim 25 10 substantially as hereinbefore described in Examples XIII or XIV.

27. A process for producing a siloxane having at least one group of the formula:



which comprises reacting ammonia or an amine having the formula:

20 HNZ_a wherein Z has the meaning defined in claim 1 with a siloxane having at least one group of the formula:

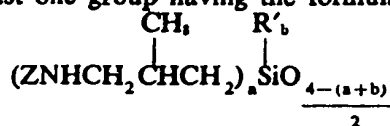


wherein R' has the meaning defined in claim 9 and a and b have the meanings defined in

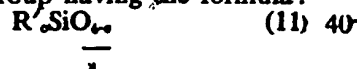
claim 1.

28. A process as claimed in claim 27 30 substantially as hereinbefore described in Example XV.

29. A process as claimed in claim 27, in which the siloxane is a copolymer containing at least one group having the formula: 35



and at least one group having the formula:



wherein R' is free from aliphatic unsaturation is a monovalent hydrocarbon group or a hydrocarbonoxy group, c is 1, 2 or 3 and Z, a and b have the meanings defined in claim 1. 45

30. A process as claimed in claim 29 substantially as hereinbefore described in Example XVI or XVII.

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Chartered Patent Agents.

Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to patents Nos. 769,498 and 822,830.